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(54) **Catalytic hydrogenation process for the manufacture of aromatic amines.**

(57) A process for the manufacture of aromatic amines comprises catalytically hydrogenating the corresponding molten nitro compound, the nitro compound having a melting point above 5°C.

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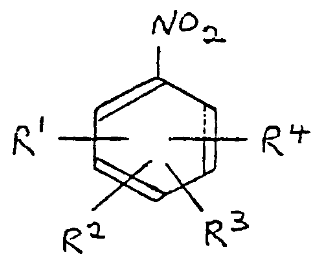
The present invention relates to the production of aromatic amines.

Aromatic amines are important starting materials for the manufacture of dyestuffs and pigments by diazotisation followed by coupling with various coupling components. It is known that aromatic amines can be prepared by catalytic hydrogenation of the corresponding nitro compound, the reactions having been performed in solution in various solvents or in the vapour phase.

We have now surprisingly found that molten aromatic nitro compounds can be reduced in the melt, giving much greater productivity and avoiding the problem of recovering the product from the solvent, which involves expensive distillation, or in handling compounds in the vapour phase. The product can be easily separated from the resulting aqueous layer and the catalyst filtered off, or in some cases, after removal of catalyst, the whole of the product mixture including the water can be used intact, e.g. to be diazotised prior to coupling.

Accordingly, the present invention provides a process for the manufacture of aromatic amines which comprises catalytically hydrogenating the corresponding molten nitro compound, the nitro compound having a melting point of above 5°C.

Suitable nitro compounds include those of the general formula:



in which R^1, R^2, R^3 and R^4 are the same or different and represent hydrogen, halogen, nitro, hydroxy, cyano, carboxyl and substituted or unsubstituted alkyl, alkoxy, aryl, aralkyl, aryloxy, or arylsulphone groups, or mixtures of such compounds.

Preferably the nitro compound is one which is solid at ambient temperatures.

The catalyst may be any that is known for carrying out catalytic hydrogenation reactions, such as nickel, platinum, palladium ruthenium and rhodium. We prefer to use palladium on charcoal as the catalyst, in suitable catalytic amounts. The amount of catalyst may be varied over a wide range and may be from 0.005% to 0.1%, based on the weight of the nitro compound. We prefer to use about 0.01%.

The reaction is carried out at a temperature above the melting point of the nitro compound being reduced and above the melting point of the resulting amine. Once the nitro compound has been melted it is not necessary to heat to a higher temperature, although this may be done if desired, for example in the case of nitro compounds having a low melting point, to increase the speed of the reaction.

The reaction may be carried out under elevated pressure which may be from 15 to 1400 psi, preferably from 70 to 420 psi.

The temperature of the reaction may be up to 150°C., preferably up to 120°C., providing that both the starting material and product are both liquid at the temperature used.

The reaction is continued until consumption of hydrogen ceases, which may take from $1\frac{1}{2}$ to 10 hours. The time taken is dependent on the temperature and pressure used in the reaction, the catalyst concentration and on the efficiency of the mixing during the reaction. For example, reaction times may be reduced by carrying out the hydrogenation in a spray nozzle high circulation reactor, such as a Buss loop reactor. Such a loop reactor normally renders an enhanced selectivity to the catalyst through more efficient mixing and cooling of the exothermic reaction. After uptake of hydrogen ceases, it is preferred to maintain the reaction conditions for an additional time, e.g. up to 30 minutes, preferably about 15 minutes to ensure that the reaction is complete.

Before the hydrogenation is started, the reactor should be purged to remove oxygen. The purging can be carried out using an inert gas, such as nitrogen or, preferably, hydrogen.

The process of the invention can be applied to various aromatic nitro compounds. These include, for example,

p-nitrotoluene, 2-nitrobenzenesulphon-N-ethylanilide and 2-nitrobenzenesulphon-N-cyclohexylamide, 2,4-dinitrotoluene, 2,6-dinitrotoluene and mixtures of 2,4- and 2,6-dinitrotoluene.

If a mixture of nitro compounds is used and it is desired to separate the resulting amines, this can be done by any desired method. For example, a mixture of 2,4- and 2,6-dinitrotoluene leads to a mixture of 2,4- and 2,6-diaminotoluene which can be separated by converting to the hydrochloride salts, fractionally crystallising and then liberating the free amine by the addition of an alkali, such as caustic soda. Additional water may be needed for the separation, in which case this may be added at the beginning and/or the end of the reduction.

The invention is illustrated by the following Examples, in which parts by weight bear the same relationship to parts by volume as do kilograms to litres.

Example 1

To a shaking autoclave was charged 451 parts by weight of molten p-nitrotoluene and a mixture of 2.25 parts by weight of catalyst comprising 5% palladium on charcoal as a 50% paste, and 10 parts by volume water (to mix the catalyst). The reactor was closed and purged with hydrogen and the p-nitrotoluene was then hydrogenated at a pressure of 70 p.s.i. and at a temperature of 100-105°C. These conditions were maintained for 4 hours when consumption of

hydrogen ceased, and then a further 15 minutes to ensure that the reduction was complete. The product was cooled to 95°C., the pressure was released and the catalyst filtered off. The autoclave and catalyst were washed with 50 parts by volume of water at 90°C. The reaction mass was collected in a separation vessel, allowed to cool to 55°C. and then settled for 5 minutes. The product formed a lower organic layer which was run off. The product, p-toluidine was obtained in a yield of 97.7% theory.

Example 2

To a shaking autoclave was charged 420 parts by weight of 2-nitrobenzenesulphon-N-ethylanilide as a melt at 95 - 98°C. and a mixture of 4.2 parts by weight catalyst comprising 5% palladium on charcoal as a 50% paste, 8.4 parts by weight sodium bicarbonate and 15 parts by volume water (to mix the catalyst). Hydrogenation was carried out at a pressure of 210 p.s.i. and a temperature of 115° - 120°C. for 4 hours after which consumption of hydrogen ceased. The reaction conditions were maintained for a further 15 minutes to ensure that the reduction was complete.

The pressure was released and the reaction mass run into a separate vessel and cooled to 75°C. 106 Parts by volume of isopropyl alcohol (as 87% isopropyl alcohol, 13% water by weight) and the mixture heated with agitation to 80°C. The catalyst was filtered off at 80°C. The catalyst and autoclave were washed with 106 parts by

volume isopropyl alcohol (87% by weight) and this was retained for the next operation.

The filtered reaction mass was run into 1800 parts by volume water at 60°C. containing 7.6 parts by weight of a dispersing/wetting agent. The mixture was cooled with rapid agitation to 25°C. to crystallise the mass. The product, 2-aminobenzenesulphon-N-ethylanilide was filtered and washed with cold water, the yield being 95.0% of theory.

Example 3

To a shaking autoclave was charged 284 parts by weight of 2-nitrobenzenesulphon-N-cyclohexylamide as a melt at 85° - 90°C. and a mixture of 1.4 parts by weight catalyst, comprising 10% palladium on charcoal as a 50% paste, 1.5 parts by weight sodium bicarbonate and 5 parts by volume water (to mix the catalyst). Hydrogenation was carried out at a pressure of 210 psi. and a temperature of 115° - 120°C. for 4 hours after which consumption of hydrogen ceased. The reaction conditions were maintained for a further 15 minutes to ensure that the reduction was complete.

The pressure was released and the reaction mass run into a separate vessel and cooled to 75°C. 62 Parts by volume of isopropyl alcohol (as 87% isopropyl alcohol, 13% water by weight) were added and the mixture heated to 80°C. with agitation. The catalyst was filtered off at 80°C. The autoclave and catalyst were washed with

62 parts by volume of 87% by weight isopropyl alcohol which was retained for the next operation.

The filtered reaction mass was run into 1220 parts by volume water at 60°C. containing 5 parts by weight of a dispersing/wetting agent, with good agitation. The mixture was cooled to 25°C. to crystallise. The product, 2-aminobenzenesulphon-N-cyclohexylamide, was filtered and washed with cold water, the yield being 97.0% of theory.

Example 4

To a shaking autoclave was charged 210 parts by volume warm water (approximately 50°C.) and 136 parts by weight of a 2,4/2,6-dinitrotoluene mixture (approx. 50:50) previously melted at about 30-35°C. The pH was adjusted to 7.0-7.5 and 2.72 parts by weight of catalyst comprising 5% palladium on charcoal as a 50% paste, were added. The reactor was closed and purged with hydrogen. The nitro compounds were then hydrogenated at a pressure of 70 p.s.i. and a temperature of 100°C. for $3\frac{1}{4}$ hours, after which consumption of hydrogen ceased. The reaction conditions were maintained for a further 15 minutes to ensure that the reduction was complete.

The reaction mass was cooled to 90°C., the pressure was released and the catalyst filtered off. The reactor and catalyst were washed with 81 parts by volume hot water and the final volume was adjusted to

406 parts.

3 Parts by volume sodium bisulphite solution (40% w/w - 25% SO_2) and 0.5 parts by weight ascorbic acid were added as antioxidants, and the temperature adjusted to 72°C. With good agitation, 97 parts by weight hydrochloric acid, S.G. 1.14 were added, during which the temperature rose to 80°C. and the pH fell to 2.5 to 3.5. At 80°C. and with slow agitation, 98 parts of sodium chloride were added over 1½ hours. The mixture was then cooled to 40°C. and filtered. The liquors contain 2,4-diaminotoluene hydrochloride.

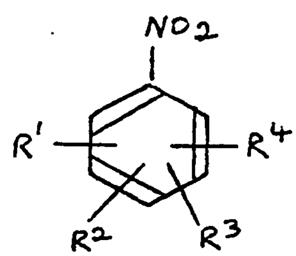
The filter cake was washed with water containing sodium chloride and ascorbic acid, the product being 2,6-diaminotoluene hydrochloride.

Each of the diamines was obtained as the free base by adding sufficient sodium hydroxide solution, at 85°C. in the case of the 2,6-isomer and 20 - 30°C. in the case of the 2,4-isomer, to render the mixture slightly alkaline. The mixture was then made neutral by adding a little dilute hydrochloric acid, and cooled to 20°C. to crystallise the diamine which was then filtered off.

What we claim is:

1. A process for the manufacture of aromatic amines which by catalytically hydrogenating the corresponding nitro compound characterised in that the nitro compound is molten and has a melting point of above 5°C.

2. A process as claimed in claim 1 characterised in that the nitro compound is one of the formula



in which R^1, R^2, R^3 and R^4 are the same or different and represent hydrogen halogen, nitro, hydroxy, cyano, carboxyl, and substituted or unsubstituted alkyl, alkoxy, aryl, aralkyl, aryloxy or arylsulphone groups, or mixtures of such compounds.

3. A process as claimed in claim 1 or 2 characterised in that the catalyst is nickel, platinum, palladium, ruthenium or rhodium.

4. A process as claimed in claim 3 in which the catalyst is palladium on charcoal.

5. A process as claimed in any preceding claim characterised in that the amount of catalyst is 0.005% to 0.1% based on the weight of the nitro compound.

6. A process as claimed in any preceding claim characterised in that the reaction is carried out at a pressure of from 15 to 1400 psi.

7. A process as claimed in any preceding claim characterised in that it is carried out in a loop reactor.

8. A process as claimed in any preceding claim characterised in that the aromatic nitro compound is p-nitrotoluene, 2-nitrobenzene-sulphon-N-ethylanilide, 2-nitrobenzenesulphon-N-cyclohexylamide, 2,4-dinitrotoluene, 2,6-dinitrotoluene or a mixture of 2,4- and 2,6-dinitrotoluenes.

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European Patent Office

EUROPEAN SEARCH REPORT

Application number
EP 78 30 0143

DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl.²)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
X	GB - A - 832 153 (ALLIED CHEMICAL CORP.) * Page 1, lines 11-34; page 2, lines 2-12 * --	1-8	C 07 C 85/11 143/80
X	US - A - 2 131 734 (C.O. HENKEL) * Examples; page 2, column 2, lines 60-66; page 3, column 1, lines 1-4 * --	1-8	
X	GB - A - 940 305 (GENERAL ANILINE & FILM CORP.) * Page 1, lines 11-19; page 2, line 94 - page 3, line 1; page 3, lines 18-28 * --	1-8	TECHNICAL FIELDS SEARCHED (Int.Cl.²) C 07 C 85/11 143/80
X	GB - A - 984 516 (ABOTT LABORATORIES) * Page 1, lines 11-17; page 2, lines 39-62; examples 2,4,5,6 * ----	1-8	

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	22-02-1979	PAUWELS